

Fine-tuning the functional properties of carbon nanotubes via the interconversion of encapsulated molecules

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(Dated: February 1, 2008)

Tweaking the properties of carbon nanotubes is a prerequisite for their practical applications. Here we demonstrate fine-tuning the electronic properties of single-wall carbon nanotubes via filling with ferrocene molecules. The evolution of the bonding and charge transfer within the tube is demonstrated via chemical reaction of the ferrocene filler ending up as secondary inner tube. The charge transfer nature is interpreted well within density functional theory. This work gives the first direct observation of a fine-tuned continuous amphoteric doping of single-wall carbon nanotubes.

PACS numbers: 73.22.-f, 78.70.Dm, 79.60.-i, 71.15.Mb

Filled single-wall carbon nanotubes (SWCNT), so called peapods, are of great research interest. Their unique nanoscale structures have a potential to bring forth novel electronic and magnetic properties. After the pioneering works of filling with C_{60} and other fullerenes or fullerene derivatives [1, 2, 3, 4], organic molecules are becoming promising candidates as a functional filler [5, 6, 7]. Since their π conjugated orbital states are highly sensitive to the chemical environments, the incorporated organic molecules can react with the surrounding, modifying the properties of the SWCNT. Specifically, organometallics are in the focus of attention as a filling material due to their large variation of the chemical properties depending upon the metal atom species. Recent theoretical studies on metallocene filled SWCNT highlighted that the variety of the metal center in between two planar aromatic ligands yields tunable carrier doping of SWCNT [8, 9, 10]. Experimentally, the filling of SWCNT with the metallocenes has been so far observed with high-resolution transmission electron microscopy (HRTEM) with cobaltocene ($CoCp_2$) [11] and ferrocene ($FeCp_2$) [12, 13]. Tube-diameter selective filling and resulting energy shifts of the corresponding fluorescence peaks were observed for the cobaltocene peapods ($CoCp_2@NT$). The HRTEM studies on a $FeCp_2@NT$ reported the conversion of the $FeCp_2@NT$ to double-wall carbon nanotubes (DWCNT) [12] or to iron clusters [13, 14]. Although these experimental works using tube materials synthesized by arc-discharge [12, 13, 14] or high-pressure CO conversion (HiPCO) methods [11] allowed ones to probe the local properties of a certain-type of individual filled tubes, it has been highly demanding to obtain a bulk scale filling of SWCNTs with a defined diameter distribution, in order to get further

insight into the bulk electronic and chemical properties and to checkup the theoretical predictions [8, 9, 10]. Very recently, the bulk-scale encapsulation of $FeCp_2$ inside SWCNTs was accomplished and an extended use of filled nanotubes in nanochemistry was proposed: the reaction process of $FeCp_2$ filler precursors towards secondary inner tube growth was identified and controlled on a bulk scale [15].

In the present work, we evidence that the reaction process of the filler molecule can be utilized for tuning the properties of SWCNT. The evolution of the chemical composition of the filler during the conversion to DWCNT is traced by observing the iron core-level absorption. The Fe 2p absorption spectra show a clear sign of encapsulated $FeCp_2$ and their decomposition by vacuum annealing, which is complementary to the previous photoemission and HRTEM study [15]. The C 1s core photoemission and absorption study unravels interactions between nanotube carbon atoms and filler molecules in the $FeCp_2@NT$, which diminish with the decomposition of $FeCp_2$. Further, a fully continuous amphoteric doping of SWCNT via chemical reactions of the filler is evidenced by tracing Van Hove singularity (VHS) peaks in valence-band photoemission. Both n-type and p-type doping of the outer tube are observed as bipolar energy shifts of the VHS peaks relative to those for the pristine SWCNT. A comprehensive analysis of the charge distribution within the $FeCp_2@NT$ and the empty DWCNT gives very good agreement between experiment and theory. This work unveils the bonding and charge transfer type interactions between carbon nanotubes and filler molecules and pioneers the use of chemical reactions of encapsulated molecules in tuning the functional properties of SWCNT. This paves the way towards nanoscale

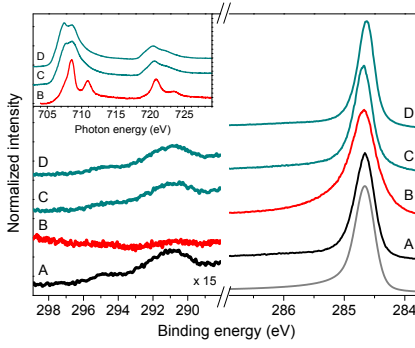


FIG. 1: C 1s photoemission spectra for samples, A. SWCNT, B. FeCp₂@NT, C. Fe doped DWCNT (600°C for 2 hours) and D. Fe doped DWCNT (600°C for 22 hours). Gray line is a Doniach Sunjic profile convoluted with Gaussian, reproducing well the C 1s peak of the SWCNT. Inset: Fe 2p absorption spectrum for the samples B, C and D.

electronic devices based on endohedrally functionalized carbon nanotubes.

The FeCp₂@NT films with a bulk filling factor of about 35 % were prepared according to the previous work [15], using the laser ablation SWCNT material with tube diameters of $1.4 \text{ nm} \pm 0.1 \text{ nm}$ [16]. A conversion of the FeCp₂@NT to the iron doped DWCNT was carried out via annealing at 600 °C in vacuum. In a similar way the same batch of the FeCp₂ was transformed into empty DWCNT by annealing at 1150 °C for 1 hour. The ultraviolet photoemission spectroscopy was performed with monochromatic He I radiation (21.22 eV) using a hemispherical SCIENTA SES 200 photoelectron energy analyzer at the IFW Dresden. The experimental resolution (better than 20 meV) and the Fermi energy were determined from the Fermi edge of clean Molybdenum substrates. The x-ray absorption experiment was carried out at beamline UE 52 PGM, Bessy II. Either drain current or partial electron yield was collected with an overall resolving power better than 10000. The base pressure in the setup was kept below 5×10^{-10} mbar. Calculations were performed using density functional theory in the local density approximation with the VASP package [17]. The cutoff energy of the plane-wave basis set was set to 350 eV. Geometry optimizations were performed until the forces on all atoms were below 0.003 eV/Å. Atomic Bader charges were evaluated using an external utility [18].

The Fe 2p absorption traces the chemical environment of the iron atoms. The inset of Fig. 1 compares the Fe 2p absorption spectra between the pristine FeCp₂@NT sample and the iron doped DWCNT samples. For the FeCp₂@NT two Fe 2p spin-orbit doublets are observed. This is very similar to the spectrum for pristine FeCp₂ observed previously [19] and evidences for the FeCp₂ molecules encapsulated without decompositions or significant modifications in structure. The iron

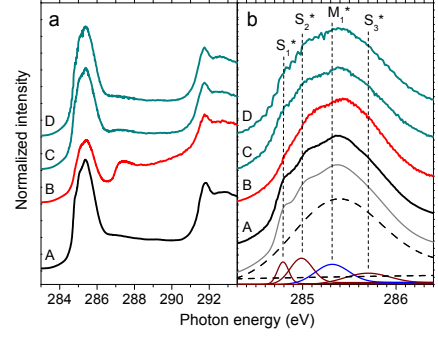


FIG. 2: a) C 1s absorption spectra for the samples A. SWCNT, B. FeCp₂@NT, C. Fe doped DWCNT (600°C for 2 hours) and D. Fe doped DWCNT (600°C for 22 hours). b) Van Hove singularity peaks at π resonance edge on an expanded scale. Gray line shows the result of line shape analysis for the SWCNT (Ref. 20).

doped DWCNT samples in turn show a set of broad and asymmetric doublets adhering to each other corresponding to variant chemical compositions of iron as observed previously with Fe 2p photoemission [15]. Such a drastic change in the Fe 2p absorption is a direct observation of decomposition of the FeCp₂ molecules.

Further, the C 1s photoemission and absorption uncovers the nature of nanotube - FeCp₂ interactions. The main panel of Fig 1 shows the C 1s photoemission spectra for the SWCNT (spectrum A), FeCp₂@NT (spectrum B) and Fe doped DWCNT samples (spectrum C and D). The C 1s main peak of the FeCp₂@NT is obviously broader and more asymmetric than that of the SWCNT. This feature is better recognized by fitting them to Doniach Sunjic profile. The derived width and asymmetric parameters are 0.175 and 0.147, respectively, which are factor 1.83 and 1.38 larger than those for the SWCNT. In turn, those for the Fe doped DWCNT samples almost recover the values for the SWCNT. Interestingly, this anomaly of FeCp₂@NT is concomitant to a decrease of the π plasmon peak located around 291 eV binding energy in the shake up region, possibly indicating reduced C π components. This is further investigated with the C 1s absorption plotted in Fig. 2a. The C 1s absorption spectrum for the pristine SWCNT exhibits π dominant peak located at photon energy around 285.4 eV and σ dominant structures above 291.8 eV. In the π peak plotted on the expanded scale in Fig 2b, the fine structures corresponding to the VHS are observed for all the samples. Those are reproduced well by the line shape analysis according to the previous work [20], as depicted at the bottom in Fig 2b. This observation confirms high purity of the samples. The C sp^2 feature consisting of the π and σ structures is drastically modified in the FeCp₂@NT. The π peak intensity relative to the σ structures is strongly reduced. Instead, a new peak appears at 287 eV. This originates from the FeCp₂ molecule which has a main peak structure

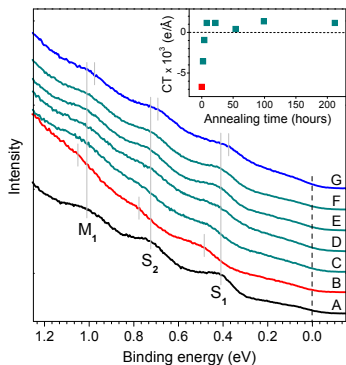


FIG. 3: He I photoemission spectra for A. pristine SWCNT, B. FeCp₂@NT, C-F. Fe doped DWCNT or FeCp₂@NT annealed at 600°C for 2, 8, 54, 212 hours, respectively, G. FeCp₂@NT annealed at 1150°C for 1 hour. Inset: annealing time dependence of charge transfer density (CT) for the outer tube in units of e/Å.

at 287 eV corresponding to C-H bonds [21]. It should be noted, however, that there must be much less pronounced features of the raw FeCp₂ observed accounting for the estimated concentration of the FeCp₂ consisting carbons [15]. In addition to the reduced π peak intensity, therefore, this can be attributed to the nanotube carbon valence states modified by FeCp₂ adsorption on the inner wall so as to project the spectral weight of the filler molecule on the C 1s absorption. The diminished fraction of the π peak is transferred to this additional peak. This also indicates stronger interaction between FeCp₂ π conjugated orbital and nanotube π orbital, which is rationalized in terms of the geometry of the π and σ orbital within the tube. Orbital mixing of the nanotube π and FeCp₂ π conjugated orbital must be responsible for this feature. This can cause a significant modification of the nanotube valence states. The features are very similar to those observed previously for hydrogenated or oxidized SWCNT [22]. In general, the additional bonding to nanotube wall yields more sp^3 like carbon atoms, which results in reducing the π dominant signal [23]. This also explains the reduced π plasmon shake up in the C 1s photoemission of the FeCp₂@NT. Additionally, those sp^3 like features observed in both photoemission and absorption diminish rapidly after 2 hours annealing, indicating the detachment of those bonding as a consequence of the decomposition of the FeCp₂ molecule as observed with the Fe 2p absorption.

We now turn to investigate the degree of charge transfer between the tube and the filler material. This is done by observing the VHS peaks in photoemission. The valence band photoemission spectrum of the pristine SWCNT exhibits three peaks corresponding to the VHS of semiconducting tubes (S_1 , S_2) and metallic tubes (M_1) [24], respectively, as shown in Fig. 3. For the FeCp₂@NT those peaks are significantly shifted towards

higher binding energies. From a close similarity to alkali metals doped SWCNT materials [25, 26], this behavior is safely attributed to the electron charge transfer from the FeCp₂@NT to SWCNT. This was reported in the previous work [15] where a charge transfer value for the FeCp₂@NT was derived from the filling factor and energy shifts of the VHS peaks by comparing them with the ones for potassium doped SWCNT. Upon annealing at 600 °C, the VHS peaks are gradually shifted towards lower binding energies and become stable after 22 hours. Surprisingly, the reached energy positions are lower than those for the pristine SWCNT. At this stage the material is transformed into the iron doped DWCNT as reported previously [15, 27]. In turn, upon 1150 °C annealing, we get the empty DWCNT, without any iron atoms, whose VHS peaks are further shifted towards lower energies. This yields a significant conclusion that there is electron transfer from the outer tube to the inner tube in the empty DWCNT. The direction of the charge transfer is the same as reported in a recent theoretical work [28, 29]. Moreover, the difference between the empty and iron doped DWCNT highlights electron charge transfer from the iron materials to the outer tubes. This electron doping should be both to the inner and outer tubes and the averaged doping level observed with VHS peak shifts depends on the chemical composition of fillers.

Finally, a quantitative analysis of the charge transfer between the filler and the SWCNT is given both experimentally and theoretically. According to the previous work [15] the number of electrons transferred from the fillers to the SWCNT was evaluated from the VHS peak shifts. The inset of Fig. 3 shows the charge transfer density (CT) of the outer tube along the tube axis for FeCp₂@NT samples annealed at 600 °C for different durations. The CT has a maximum minus value of -0.0067 e/Å for the pristine sample and drops rapidly at the first few annealing steps and becomes plus constant around +0.0010 e/Å after 8 hours annealing. In contrast, the iron concentration is much less dependent of annealing and shows only a factor 0.7 drop in the end. These features suggest that the chemical status of the filler material is certainly responsible for the evolution of the CT. For the representative two filled samples, FeCp₂@NT and the empty DWCNT, the possible filled structures are available [15], thus, the CT for the actual samples can be extrapolated to those for 100 % filled materials. The results are -0.0180 e/Å for FeCp₂@NT and +0.0286 e/Å for DWCNT.

On the theoretical side, we have calculated the CT between ferrocene and a host (9,9) nanotube. This tube has a diameter which is a good representation of our experimental sample and is highly suited for optimal ferrocene filling. We have examined both the case of the standing and the lying FeCp₂, assuming van der Waals distance between the FeCp₂ and the nanotube wall. The geometries of the nanotube and the FeCp₂ were opti-

mized separately, and the optimal distance between them was obtained by finding the minimum of the total energy as a function of the distance. A full geometry optimization was performed subsequently, but no essential change was found in the CT values. Both ferrocene alignments yielded a transfer of electrons from the FeCp₂ to the nanotube, in full agreement with the measurements. For the standing and lying geometry, the CT was found to be -0.0020 e/Å and -0.0029 e/Å, respectively, far less than the experimental -0.0180 e/Å. In comparison, we have also calculated the CT for the case of the (4,4)@(9,9) DWCNT, which yielded $+0.0065$ e/Å for the outer wall. Once again, the direction of the charge transfer is in full agreement with the experiment, and in this case the magnitude is also closer. It should be noted that a previous study [28, 29] has revealed that the inter-molecular Hückel model [30] yields about a factor 2 larger magnitude for the CT in double walled tubes than the LDA does; in the case of the (4,4)@(9,9) the CT was found to be $+0.0138$ e/Å with this model. The latter value is much closer to the experimental value of $+0.0286$ e/Å.

In the case of the ferrocene filled tubes, even applying a factor 2 correction yields far too low CT. This discrepancy might suggest that the FeCp₂ effectively binds into the tube wall: the theoretically considered scenario – i.e. van der Waals distance between the FeCp₂ and the nanotube wall – allows only for weak inter-molecular interactions leading to small CT, while a strong – possibly covalent – bonding may allow for a larger CT between the two subsystems. We have performed further calculations to examine this possibility by studying a simple test geometry in the parallel orientation where the 2 hydrogens nearest to the tube wall are removed from the FeCp₂ which then binds into the wall by the thus appearing dangling bonds [31]. We found that in this geometry the CT is indeed much greater, and the carbon atoms of the nanotube which are involved in the bonding are of largely sp^3 character. The latter result also agrees with our aforementioned C 1s core-level measurements which showed that some of the carbon atoms in the tube wall have a strong sp^3 character, indicative of orbital hybridization between the subsystems. Thus, both (i) the discrepancy between the measured and calculated CT and (ii) the sp^3 character of carbon atoms found by C 1s spectroscopy, suggest in unison that there should be some kind of relatively strong, possibly covalent bonding between the FeCp₂ and the host nanotube. This is essentially an indication of possible endohedral functionalization of the nanotube, which has been suggested to be theoretically possible recently [32].

In summary, we have evidenced the potential of filling and subsequent chemical reactions to tune the properties of SWCNT. Both n-type and p-type doping of the SWCNT were achieved from different chemical states of the filler. Good agreement was found between the experimental and theoretical CT values. Our results show that

covalent and noncovalent interactions are responsible for the endohedral functionalization of the SWCNT.

This work was supported by the DFG Pl 440/3/4, by OTKA grants no. K60576 and F68852, Hungary, by a Grant-in-Aid for Scientific Research A (No.18201017) by the Ministry of Education, Culture, Sports, Science and Technology of Japan. H. S. acknowledges the Alexander von Humboldt Foundation. C. K. acknowledges the IMPRS. A. G. acknowledges an individual Marie Curie fellowship. V. Z. acknowledges the Bolyai fellowship. We thank R. Hübel, S. Leger, R. Schönfelder and H. Klose for technical assistance.

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